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THE EFFECT OF GAS MEDIUM ON GLASS SURFACE CRYSTALLIZATION (A Review)

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The possibility of modifying the surface properties of glass ceramics via crystallization of glass in a controlled gas medium is demonstrated. The main gas reactants and their effects in heat treatment of glass are analyzed. Technological parameters of using gas agents are considered, and service qualities of glass ceramic materials with modified surfaces are discussed.

Contemporary industrial technologies call for development of new materials with a combination of high-quality service parameters. Glass justifiably belongs to such materials. The required properties can usually be obtained by altering the chemical composition of glass, which often involves technological difficulties and is not economically feasible. As a rule, in order to significantly change various properties of glass or glass ceramics, it is sufficient to modify the surface layer of the material. The currently used technologies of ion exchange, surface pickling, and coating application require significant changes in the technology and, accordingly, substantial expenses. An efficient method for modifying the surface layer of glass ceramics consists of using a controlled gas medium in the glass crystallization process.

Numerous studies are dedicated to chemical interaction of glass and gases. Most of these results are analyzed in [1]. It is obvious that with changes in the chemical composition and structure of the glass surface layer, its crystallization will proceed in a special way. At the same time, studies of the effect of the gas medium on the crystallization of the glass surface are limited.

The present paper describes the main results regarding this important problem which were obtained by foreign researchers and the author of the paper and which make it possible to analyze and deliberately use a specific gas medium in each specific case.

The depth and the extent of structural transformations in the surface layer of glass ceramics depend on the type of the gas reactant, the glass chemical composition, and the heat treatment conditions.

Gas reactants can be arbitrarily split into several groups depending on their effect on the glass surface:

SO_2 , SO_3 , HCl , CCl_4 , CH_2Cl_2 , CF_2Cl_2 , CO_2 and others react to glass components and form the corresponding reaction products on its surface; the reaction products mostly include univalent, less often, bivalent cations; the chemical resistance, microhardness, and surface electric resistivity of these materials are increased due to dealkylation and structure compaction;

H_2 , H_2S , natural gas, O_2 , and others change the degree of oxidation of the surface layer ions; as a consequence of reduction, the valence of Pb^{2+} , Bi^{2+} , Fe^{3+} , Mn^{4+} can be decreased to the metallic state; the glass surface becomes conducting; a change in ionic equilibrium significantly affects the crystallization properties;

N_2 , NH_3 , F_3 are gases which do not chemically interact with glass surface, but as a consequence of in-depth penetration can replace OH^- or O^{2-} groups in the glass structure; mechanical properties and chemical resistance are improved due to the condensation of the structure;

Ar and He do not react chemically with glass components and contribute to protecting the surface from air oxygen oxidation; treatment of glass under pressure can improve mechanical properties.

Patents of Great Britain (1151770, 1303799) and the USA (4042362) describe production of glass ceramics using on SO_2 or SO_3 atmosphere. In crystallization of glasses of the $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{Li}_2\text{O}$ system in moist SO_2 medium, a glass ceramic material with a polished glossy surface was obtained (Gr. Britain 1151770). The surface layer thickness did not exceed 10 μm . In this case the molded article was treated with the specified gas at an increased temperature.

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Due to diffusion of the lithium ions to the glass surface layer, a reaction took place and lithium sulfate was formed on the glass surface in the form of a thin white tarnish which was easily removable. Due to the decreased lithium concentration in the surface layer, this layer on subsequent heat treatment remained vitreous while the rest of the sample body was a glass ceramic.

When other glass compositions were used (patent of Gr. Britain 1303079, USA 4042362) [2] such treatment either caused strengthening of the glass ceramic (if the difference in the CTLE of the surface and the middle layer was significant) or improved its chemical resistance.

When iron-bearing glass of the pyroxene composition was treated in SO_2 medium, easily washable products in the form of simple and complex sulfates of sodium, potassium, calcium, and iron were formed on the glass surface within the temperature range of the endothermic effect (according to the DTA curve) [2]. After the removal of these sulfates the glass ceramic material had a shiny glossy surface of black color, whereas in air it had a brown color. Electron microscope analysis revealed a surface layer 12 μm thick that has a vitreous structure. The IR reflection spectra of the glass and the obtained glass ceramic were virtually identical. However, both maxima in the glass ceramic IR spectrum are shifted toward an increase in the wave number, which points to an increased amount of $\text{Si}-\text{O}-\text{Si}$ bridge bonds. Owing to this, the obtained glass ceramic exhibits high chemical stability.

The effect of CO_2 on the glass surface is significantly smaller than that of SO_2 and is often questioned. It depends on many factors and, in particular, on the gas moisture and the chemical composition of the glass. Thus, as the two-component glass of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ in [3] was treated with moist CO_2 , Na_2CO_3 crystals were formed on the surface, which later initiated crystallization of the glass surface layer. The rate of crystal growth was significantly higher than in air or in nitrogen medium.

The author of the paper subjected alkaline iron-bearing glass containing 17 wt.% ($\text{FeO} + \text{FeO}_3$) to carbonic acid treatment. As the result, reaction products represented by crystals whose size increased with increasing temperature of the treatment were detected on the surface. Thus, at the temperature of 500°C the crystal size is 0.1–1.4 μm , and at 650°C it is 5–8 μm . At 700°C the crystals merge. It is established that Na^+ ions are present in the composition of the resulting products, and at a higher heat treatment temperature, K^+ and Ca^{2+} are present as well, and their amount grows as the temperature increases. The tarnished glass powder crystallizes more intensely than the untarnished glass, which is supported by the nature of the DTA curve. Consequently, the crystals emerging as the reaction products create an additional phase boundary on the glass surface, which catalyzes the crystallization process and intensifies its course. As the result of the mentioned heat treatment of the glass, the composition and structure of the glass ceramic surface layer are modified. Owing to this, the water resistance of the glass ce-

ramic surface increases more than twice and the wetting contact angle decreases by 8–10° as compared to the glass ceramic obtained in air [4].

Several researchers synthesized glass ceramics in a reducing medium (USA pat. 3962514, France 2147115) [5]. Such atmosphere is mostly used when the glass composition includes variable-valence oxides, in particular, iron oxides. The author of patent 3962514 (USA) heat-treated glass in a reducing atmosphere. The gas reactants were H_2 , ($\text{H}_2 + \text{N}_2$), CO , Cl_2 , S, methane, and hexane. A spinel film possessing electrical and magnetic properties emerged on the glass ceramic surface.

When glass containing iron ions is crystallized in an $\text{H}_2 + \text{N}_2$ atmosphere, the equilibrium of $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$ in the surface layer is shifted to the right. As the result of the changes, the extent of crystallization in this layer is significantly higher than in the rest of the sample. The surface layer passes to the compressed state and, consequently, the mechanical strength of the glass ceramic increases (pat. France 2147115). However, in other studies [5] the surface layer does not crystallize during crystallization of iron-containing glasses in a reducing medium and remains vitreous.

The study in [6] investigated the thermal hydrogen treatment of highly ferrous glass of the pyroxene composition in the production of glass ceramics. The glass was treated in a quartz reactor located inside an electric furnace; hydrogen was supplied to the reactor from a cylinder starting at 100°C. The glass crystallization according to this scheme yielded a black glass ceramic material with a mirror-like surface. The x-ray phase analysis of the surface layer revealed the existence of structural groups enriched with metallic iron. The IR reflection spectrum is similar in its nature to the IR spectrum of the original glass; however, the main maxima are shifted towards the high-frequency range [7]. The study of this material with a microscope confirmed the absence of any crystalline inclusions and the presence of a multilayer composite structure.

Thus, the surface layer of the obtained glass ceramic has the vitreous structure with an increased content of SiO_2 and the inner part of this layer is enriched with metallic iron. The main glass ceramic layer is located under it. The total thickness of the modified layer is 0.4–0.6 μm . It should be noted that the water resistance of the surface is 10 times higher than the same parameter in the glass ceramic obtained in air. The microhardness varies insignificantly.

Oxygen in limited quantities is capable of physical dissolution in glass. The highest degree of solubility is found in quartz glass. If there is a shortage of oxygen ions in the glass, heat treatment in the oxygen medium intensifies the crystallization process [8]. A similar situation was observed in [9], and in the presence of moisture this effect was more pronounced. A significant effect of oxygen was observed in crystallization of fluoride glasses [10]. It was established that the presence of oxygen has a substantial effect on the nature

of the crystalline phase and an excess of it can even lead to stratification of the glass.

The author investigated the process of crystallization of glass containing (%): 74.0 SiO₂, 8.0 CaO, 18.0 Na₂O in oxygen supplied from a cylinder. The experimental and calculated data indicate that under short-term holding (up to 30 min) in the said environment, no special effect was observed. Only the holding of glass above 30 min increases the size of the crystals compared to holding in air. It can be assumed that the reason for this is similar to the one noted in [8].

Thermal gas treatment of optical glass in a nitrogen medium [11] is accompanied by the transformation of the composition and structure of the surface layer, which causes modifications of physicochemical and service properties. Nitrogen in thermal gas treatment is incorporated in the glass surface layer to a depth of 60 – 100 nm by ionic replacement of the bridge – O – and non-bridge = O oxygen by two and three coordinate nitrogen, which results in the emergence of cross-lateral bonds between the structural chains and increases the extent of bondedness of the glass-forming skeleton and compaction of the surface layer. It should be noted that even a slight quantity of nitrogen in glass (6 mole %) substantially decreases the crystallizing ability, increases chemical resistance and microhardness, and decreases the TCLE [12].

The author performed thermal analysis of glass of the Na₂O – CaO – SiO₂ system in an argon medium. The nature of the resulting thermograms makes it possible to state that the intensity of the thermal effects observed in glass crystallization substantially decreases, as compared to the thermal effects observed in crystallization of glass in an air medium. This is another evidence of the active role of oxygen and moisture in the crystallization process.

The effect of water steam should be mentioned separately. The study in [9] was related to crystallization of quartz glass in dry and moist media of oxygen, argon, and air. It is established that crystallization proceeds much more intensely in all moist media. Other researchers came to the same conclusion [3, 13]: the rate of growth of crystals in the moist gas is 3 – 5 times higher than in the dry gas. The authors attribute this fact to the formation of OH[–] groups and their incorporation into the destroyed complexes Si – O – Si. As the result of incorporation of the OH[–] groups into the glass structural lattice, the viscosity and surface tension decrease, which accelerates the formation of crystallization centers and the growth of crystals [14, 15].

Thus, the mentioned experimental data support the fact that the gas medium is one of the determining factors affecting the nature and kinetics of crystallization in the glass surface layer. A deliberate and expedient choice of a specific gas reactant makes it possible to expand the possibilities for producing glass ceramics with prescribed surface properties.

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